Mesoporous tantalum oxide as catalyst for dehydration of glucose to 5-hydroxymethylfurfural

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ABSTRACT

Mesoporous tantalum oxide was prepared by acid hydrolysis of tantalum penta-ethoxide in the presence of a triblock co-polymer Pluronic L-121, a non-ionic surfactant, at room temperature and subsequent calcination at 550 °C for 6 h. This solid exhibits a suitable specific surface area (79 m^2 g^{-1}) and a high acidity (353 μmol NH$_3$ g^{-1}) with the presence of both Brönsted and Lewis acid sites, demonstrating to be active as solid acid catalyst in the dehydration of glucose to 5-hydroxymethylfurfural (HMF), in a biphasic water/methyl-iso-butyl ketone (MIBK) system. Thus, by using a glucose:catalyst weight ratio of 3:1, a glucose conversion of 69% and a HMF yield of 23% were achieved at 175 °C, and after only 90 min of reaction time. The catalytic process is selective toward HMF, which is preserved from ulterior hydration to levulinic acid. Fructose was also detected as by-product of glucose isomerisation with 14% of selectivity. The catalyst is very stable, since no leaching of tantalum species to the liquid phase was found; moreover, the catalytic performance of this acid solid is well recovered after calcination at 550 °C for 2 h.

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1. Introduction

The increasing oil prices and the diminishing fossil fuel reserves, as well as the growing concern about global warming, have led to the search of new sustainable sources of energy from renewable materials. Biomass can be considered as a renewable feedstock that can be used for fuel and chemical production, taking advantage from its abundance and relative low cost. For instance, platform chemicals and biofuel production from waste lignocellulosic biomass is an attractive alternative to fossil-based feedstocks. The main products obtained from agriculture waste and energy crops consist of cellulose (40–50%), hemicellulose (25–35%) and lignin (5–20%), being glucose the building block of cellulose [1]. High glucose yields are achieved via enzymatic hydrolysis of cellulose, although it can be also carried out under harsher conditions using solutions of mineral acids at elevated temperatures.

Among current biofuel sources, one of the most important building blocks is 5-hydroxymethylfurfural (HMF) obtained from biomass, which is a versatile and key intermediate for the production of a wide variety of biobased chemicals [2]

(e.g. levulinic acid, furandicarboxylic acid, dimethyl furan, γ-valerolactone and dihydroxymethylfurfural) and it is attracting much attention in biofuels and chemical industry [3,4]. HMF can be easily prepared by triple dehydration of fructose catalysed by mineral acids; however, starting from saccharides, special catalysts are required to perform the glucose dehydration to HMF.

Besides mineral acids, other catalysts have been employed to obtain HMF, such as metal salts in non-aqueous solvents (DMSO) [5], Lewis acids from different metallic salts in acid medium [6], lanthanide salts in biphasic solvent systems [7] or in ionic liquids [8]. However, all these catalytic systems have important drawbacks associated to the high cost of ionic liquids and high energy consumption in the case of organic solvents. For industrial applications, heterogeneous catalysts are recommended due to their low cost and their easy recovery from reaction medium. Recently, several compounds based on elements of the 5th group of the Periodic Table have been employed as catalysts for the preparation of HMF. Thus, the so-called "niobic acid" (Nb$_2$O$_5 \cdot n$H$_2$O) is an amorphous solid with strong acidic properties due to the presence of highly polarized water molecules, which has been used for dehydration of mono- and polysaccharides to HMF at 160 °C in a biphasic water-2-butanol system, attaining a HMF yield of 46% from glucose [9]. This solid was also studied by Carniti et al. [10] in this reaction,

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observing the absence of side-reaction in the dehydration of fructose to HMF in water at 100 °C. This catalytic activity of $Nb_2O_5 \cdot nH_2O$ has been mainly attributed to the presence of water tolerant Lewis acid sites [11].

Moreover, a surface treatment of niobic acid with phosphoric acid led to an enhancement of the surface acidity, and therefore of its catalytic activity [12,13]. Different works have dealt with this niobic acid promoted with phosphoric acid catalyst, under batch conditions at 110 °C [14,15], or in a continuous reactor line at 90–110 °C [16]; all of them have reported high catalytic activity in the selective fructose dehydration to HMF. This high activity is justified by a synergy effect between a protonated phosphate group and a nearby metal Lewis acid site [17].

In a similar way, hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$) displays strong acidity in its amorphous form and good activity in the dehydration of fructose at 160 °C [18]. The catalytic performance is clearly improved when this solid is treated with phosphoric acid at 300 °C, achieving a HMF yield of 58% when the substrate was glucose.

The aim of the present work is the preparation of a mesoporous tantalum oxide and its application to the dehydration of glucose to HMF in a biphasic water/methyl-iso-butyl ketone system. The use of ordered mesoporous catalysts presents significant advantages with respect to conventional ones, due to their high specific surface area and large pore size, which lead to a better diffusion of reactants and products [19]. In this study, the influence on the catalytic behavior of different experimental parameters, such as reaction temperature and time, percentage of catalyst and reutilization, has been evaluated in order to attain high HMF productivity values.

2. Experimental

2.1. Synthesis of mesoporous tantalum oxide

Mesoporous tantalum oxide was synthesized via a surfactant-assisted sol–gel process, in a similar way to the reported synthesis of other mesoporous oxides of niobium and tantalum [20,21], but following the modification introduced by Xu et al. [22]. Thus, a tri-block co-polymer Pluronic L-121 (Sigma-Aldrich) and $Ta(OC_2H_5)_5$ were employed as structure-directing agent and inorganic precursor, respectively. In a typical synthesis, 1 mmol of tantalum penta-ethoxide and 2 mL of 2 M hydrochloric acid aqueous solution were added to an ethanol solution containing 0.25 g of surfactant, under inert atmosphere. After stirring for 30 min, the resulting gel was aged at 40 °C for 24 h. Finally, the gel was dehydrated under vacuum at 60 °C to obtain a white solid. The surfactant was eliminated by calcination at 550 °C for 6 h. The obtained mesoporous tantalum oxide was kept in equilibrium with an atmosphere of 55% humidity.

To improve the acidity of this mesoporous tantalum oxide, 1 g of this solid was treated with a 1 M H_3PO_4 aqueous solution for 24 h, at room temperature. After drying at 60 °C, the solid was calcined at 300 °C for 2 h. Another catalyst was prepared in a similar way, but drying the sample at 85 °C for 2 h, without the calcination step.

2.2. Characterization techniques

Powder X-ray diffraction (XRD) patterns of catalysts were obtained on a PAN analytical X'Pert Pro automated diffractometer. They were recorded in Bragg-Brentano reflection configuration by using a Ge (1 1 1) primary monochromator (Cu $K\alpha_1$) and the X'Celerator detector with a step size of 0.017° (2θ), between 10° and 70° in 2θ with an equivalent counting time of 712 s step^{-1}. To investigate the formation of possible crystalline phases from

mesoporous tantalum phosphate a thermodiffractometric study was carried out using an Anton Paar HTK1200 Camera under static air. A gas flow was not employed to avoid sample dehydration prior to the diffraction experiment. Data were collected at temperature intervals of 100 °C, ranging between 100 and 900 °C with a heating rate of 10 °C min^{-1}, and maintaining 15 min at each temperature to ensure thermal stabilization. The data acquisition range was 8–70° (2θ), with a step size of 0.017°.

Thermogravimetric (TG) and differential thermal analysis (DTA) of catalyst precursors were performed from room temperature until 850 °C on a SDT Q600 apparatus from TA Instruments, by using calcined alumina as reference and a heating rate of 10 °C min^{-1}. Textural properties of catalysts were obtained by nitrogen adsorption at liquid nitrogen temperature with a Micromeritics ASAP 2010 apparatus, after degassing the samples at 350 °C overnight. The accumulated pore volumes were determined by BJH method. Temperature programmed desorption of ammonia (NH_3-TPD) was used to determine the total acidity of the samples. Before the adsorption of ammonia at 100 °C, samples were heated from room temperature to 550 °C, with a heating rate of 10 °C min^{-1} and maintaining the sample at 550 °C for 1 h. The NH_3-TPD was performed between 100 and 550 °C with a heating rate of 10 °C min^{-1}, and the amount of desorbed ammonia was analyzed by an on-line chromatograph provided with a TC detector. FTIR spectra of adsorbed pyridine were recorded on a Shimadzu Fourier Transform Infrared Instrument (FTIR-8300). Self supported wafers of the samples with a weight/surface radio of about 15 mg cm^{-2} were placed in a vacuum cell greaseless stopcocks and CaF_2 windows. The samples were evacuated at 150 °C and 10^{-2} Pa overnight, exposed to pyridine vapors at room temperature for 15 min and then outgassed at different temperatures. Raman spectra were obtained with a Raman Senterra (Bruker) micro-spectrometer equipped with a thermo-electrically cooled CCD detector. Excitation radiation at 1064 nm was used as supplied from a Praseodimium laser. Raman spectra were performed from powder samples without any previous treatment.

X-ray photoelectron spectra were obtained using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Al K_α radiation (300 W, 15 kV, 1486.6 eV) with a multi-channel detector. High resolution spectra were recorded at 45° take off-angle by a concentric hemispherical analyzer operating in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was done against adventitious hydrocarbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian–Lorentzian curves in order to determine more accurately the binding energy of the different element core levels.

2.3. Catalytic test

For the dehydration reaction of glucose, a two-phase reactor system, consisting in water-MIBK, was used. MIBK was introduced to promote the dehydration reaction by shifting the equilibrium toward the formation of HMF, by extracting it immediately under stirring. In this way, HMF degradation can be avoided [23,24]. The catalytic reaction was carried out in a glass reactor of 15 mL, provided with a screw top of Teflon, at 175 °C and 90 min of reaction time, with a stirring rate of 600 rpm. Zero time was taken when temperature of the reactor reached 175 °C. The reaction was performed by using 50 mg of catalyst, 0.15 g of substrate in deionized water (1.5 g) and 3.5 mL of MIBK. After reaction time, this was quenched by introducing the reactor in a bath with cooled water; the liquid phases were separated and filtered, and the analysis of products was done in both phases. Glucose conversion and the product selectivity were calculated according to the following
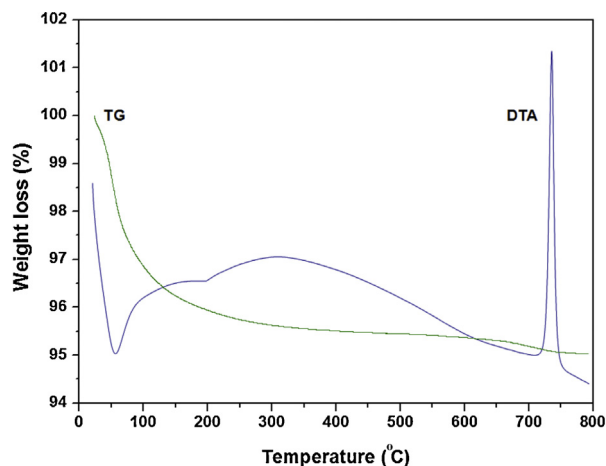
Fig. 1. TG and DTA curves of mesoporous tantalum oxide.

Fig. 2. (A) XRD patterns at low angles and (B) at high angles of mesoporous tantalum oxide.

equations:

glucose conversion(wt%)

$$= \frac{\text{mass of starting glucose} - \text{mass of remaining glucose} \times 100}{\text{mass of starting glucose}}$$

$$\text{product selectivity(mol\%)} = \frac{\text{moles of produced product} \times 100}{\text{moles of glucose reacted}}$$

Both the aqueous and the organic layers were analyzed by high performance liquid chromatography (HPLC), by using a JASCO liquid chromatograph equipped with quaternary gradient pump (PU-2089), multiwavelength detector (MD-2015), autosampler (AS-2055), column oven (co-2065) using a PHENOMENEX LUNA C18 reversed-phase column (250 mm × 4.6 mm, 5 µm) and PHENOMENEX REZEX RHM-Monosaccharide H$^+$ (8%) C18 (300 mm × 7.8 mm, 5 µm). The disappearance of glucose was monitored using a refractive index detector while HMF production was monitored using a UV detector. Glucose conversion and HMF selectivity were calculated using the volumes of aqueous and organic phases used in the reaction. The solvents were filtered through a 0.45 µm filter and degassed with helium prior use. Methanol (flow rate 0.5 mL min^{-1}) and water (flow rate 0.6 mL min^{-1}) were used as mobile phases in LUNA C18 and REZEX RHM columns, respectively. Injection volumes were of 6 µL, and the columns temperature was held constant at 80 °C. All samples were dissolved in methanol (LUNA C18) or water (REZEX RHM)

3. Results and discussion

3.1. Characterization of mesoporous tantalum oxide

The TG curve of the mesoporous tantalum oxide, after calcination at 550 °C and kept in equilibrium with an atmosphere of 55% humidity, shows two weight loss steps between room temperature and 600 °C (Fig. 1). The first one extending till 175 °C (2.90 wt%) is due to the elimination of humidity retained in the solid, and it is associated to the endothermal effect observed in the DTA curve between 50 and 150 °C. The second weight loss, between 175 and 600 °C (0.76 wt%), is originated by the elimination of OH groups and water molecules coordinated to the tantalum ions. These data clearly indicate that OH groups and coordinated water molecules are strongly retained by the tantalum atoms, since they require high temperatures to be eliminated [25]. According to these weight losses, the chemical composition for this solid is $Ta_2O_5 \cdot 0.19\,H_2O$. Although $Ta_2O_5 \cdot nH_2O$ prepared from the hydrolysis of $TaCl_5$ exhibits better acidic properties when is calcined at
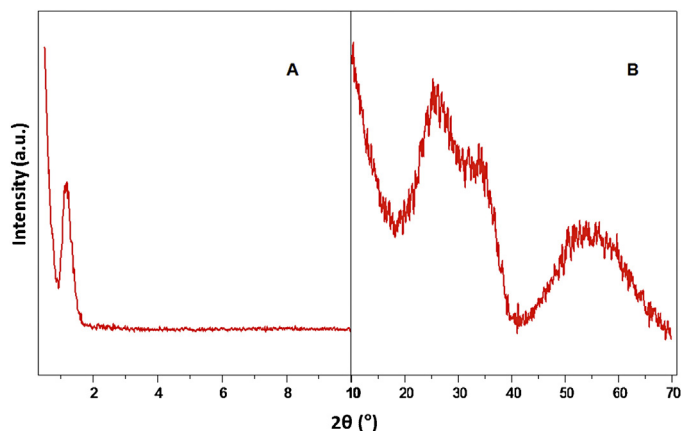
moderate temperatures, 200–400 °C [26], the use of a surfactant to prepare mesoporous tantalum oxide makes necessary calcination temperatures as high as 550 °C, in order to remove all the surfactant molecules. Consequently, the number of water molecules retained by this mesoporous solid is very low, 0.19 H_2O per formula, but enough to confer acid properties to this catalyst [26]. Finally, in the DTA curve is observed a sharp exothermal peak, which could be assigned to the formation of crystalline Ta_2O_5.

The X-ray diffraction pattern in the low-angle region of the mesoporous tantalum oxide exhibits an intense peak centred at $2\theta = 1.2°$, typical of a mesoporous structure (Fig. 2). Thus, the corresponding interplanar d_{100} spacing, assuming a hexagonal arrangement, is 7.36 nm. From this d_{100} value, the hexagonal unit cell parameter a_0 can be determined by using the following equation: $a_0 = 2\,d_{100}/\sqrt{3}$. The a_0 value obtained is 8.5 nm and represents the sum of the pore diameter (which can be obtained from the nitrogen adsorption–desorption isotherms) and the oxide wall thickness (w_t). Since the average pore diameter is 3.3 nm (*vide infra*), the wall thickness of this mesoporous tantalum oxide is 5.2 nm. In the high-angle region, no diffraction lines were detected (Fig. 2), except three large bands at 25°, 33° and 55°, associated to the amorphous walls of this solid.

A thermodiffractometry study of the mesoporous tantalum oxide, once the surfactant was eliminated by calcination at 550 °C, was performed between room temperature and 1000 °C (Fig. 3). All the diffractograms obtained at temperatures lower than 500 °C do not evidence any diffraction signal in the high-angle region, thus
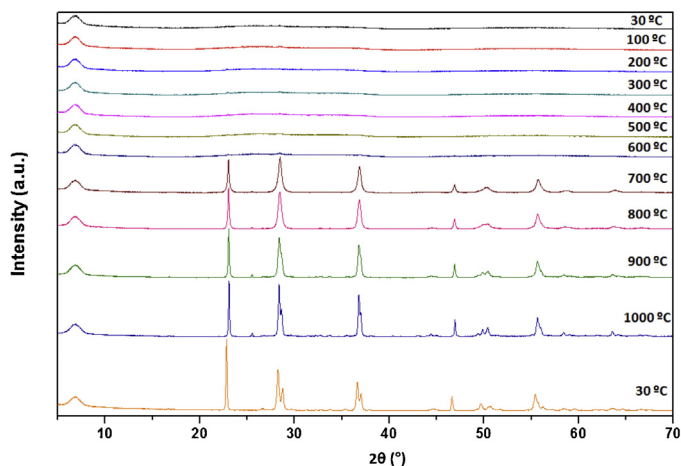

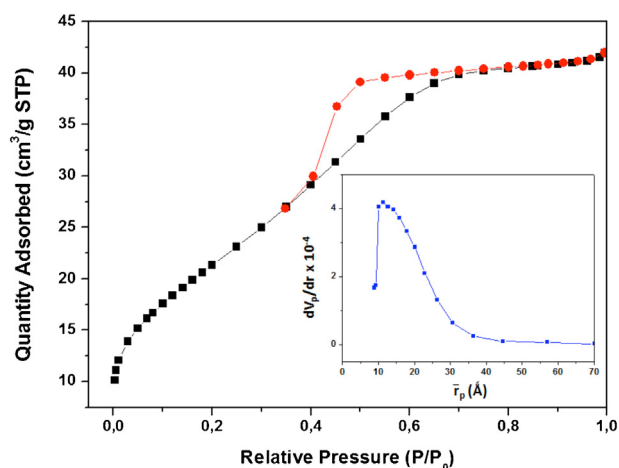**Fig. 3.** Thermodiffractometric study of mesoporous tantalum oxide.

Fig. 4. Adsorption–desorption isotherms of N$_2$ at −196 °C of mesoporous tantalum oxide.

Fig. 6. FTIR spectrum of mesoporous tantalum oxide at room temperature.

revealing the absence of crystalline phases. However, at temperatures higher than 600 °C, well defined diffraction peaks appear at 22.8°, 28.2° and 36.5°, 46.5° and 55.3°, corresponding to the β form of orthorhombic Ta$_2$O$_5$ [27]. This fact means that at this temperature the mesoporous structure is destroyed and leads to the formation of a crystalline tantalum oxide. At the highest temperature, the peaks at 28.2° and 36.5° are split, revealing the increase in crystallinity with a more drastic thermal treatment.

The textural parameters of mesoporous tantalum oxide were obtained from N$_2$ sorption at −196 °C. The N$_2$ adsorption–desorption isotherm of this solid belongs to the type IV in the IUPAC classification, typical of mesoporous solids (Fig. 4). The BET surface area value is 79 m^2 g^{-1}, with a average pore diameter of 3.3 nm. The pore size distribution (inset of Fig. 4) exhibits a large band extending from 1 till 3 nm of pore radii.

The Raman spectrum of mesoporous Ta$_2$O$_5$ is shown in Fig. 5. This spectrum, in the range 200–1200 cm^{-1}, presents a major characteristic Raman band at 660 cm^{-1} due to Ta–O stretching vibrations of TaO$_6$ octahedra [28]. The shoulder observed at about 940 cm^{-1} corresponds to the symmetric stretching mode of some terminal Ta=O bonds [29]. In the corresponding FTIR spectrum of this solid, a peak at 2335 cm^{-1}, which can be assigned to Ta–O–Ta stretching vibrations [29], also appears, together with peaks at 1615 and 3400 cm^{-1} associated to the vibration modes of water molecules and OH groups present in the solid (Fig. 6).
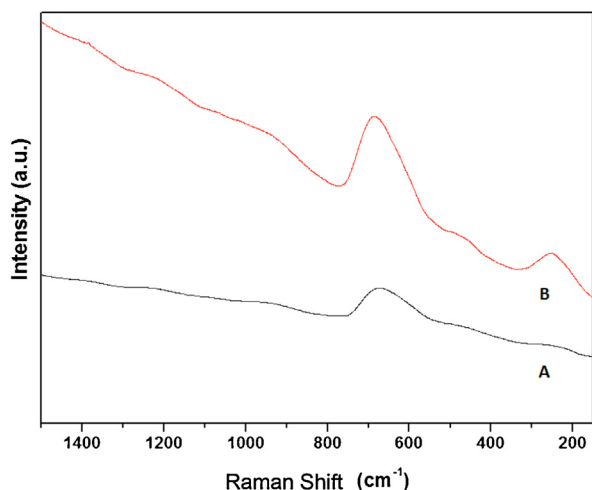
In order to get insights into the surface composition of this mesoporous solid, X-ray photoelectron spectroscopy was employed for its characterization. In the core level region of tantalum, two peaks corresponding to Ta 4f$_{7/2}$ and Ta 4f$_{5/2}$ are observed (Fig. 7) at 26.1 and 28.0 eV, respectively [30,31]. The binding energies separation close to 1.9 eV and the area ratio of 1.36 confirm that Ta is fully oxidized as Ta(V). On the other hand, the O 1s signal appears as an intense band centred at 531.6 eV with a large tail at high energy; this band can be deconvoluted in two components at 530.5 and 531.9 eV (Fig. 7), which points to the existence of two different oxidic environments: oxygen forming the Ta$_2$O$_5$ network, and therefore bonded as Ta–O–Ta (530.6 eV), and oxygen belonging to coordinated water or coordinated OH groups (532.3 eV), respectively [32].

The acidity of this mesoporous tantalum oxide was measured by NH$_3$-TPD. The total acidity is high, attaining 353 μmol NH$_3$ g^{-1}, being 34.8% of the total ammonia molecules desorbed at temperatures above than 300 °C. Therefore, it can be considered as a strong acid solid. Taking into account that, previous to the adsorption of ammonia, the catalyst was treated at 550 °C during 1 h, the loss of a majority of coordinated water molecules takes place, so that the amount of desorbed ammonia could correspond with the number of tantalum atoms able to coordinate an ammonia molecule. Thus, the total acidity value leads to the following chemical composition: Ta$_2$O$_5$ 0.16 NH$_3$. The number of ammonia molecules is almost coincident with that found for the coordinated water (0.19 mol mol^{-1} of oxide), thus confirming that the acidity of this solid is mainly originated by the presence of coordinated water molecules and coordinated OH groups to tantalum ions.

3.2. Catalytic study

The mesoporous Ta$_2$O$_5$ has been evaluated as acid catalyst in the reaction of dehydration of glucose to HMF in a biphasic water/methyl-iso-butyl ketone system. First, the influence of the reaction temperature on the catalytic activity has been evaluated. The experimental conditions were: 50 mg of catalyst, 90 min of reaction time. The catalytic results reflect that glucose conversion rises with temperature, achieving a value close to 76.5% at 185 °C (Fig. 8). Only fructose and HMF were found as reaction products, being the former favored at low temperatures, whereas the selectivity to HMF increases up to 175 °C. Levulinic acid was never detected. Above this temperature, the selectivity to HMF decreases due to the rapid formation of soluble polymers and humins on the catalyst surface, which are then favored. That means that glucose is rapidly isomerized, in a first step, into fructose, which is
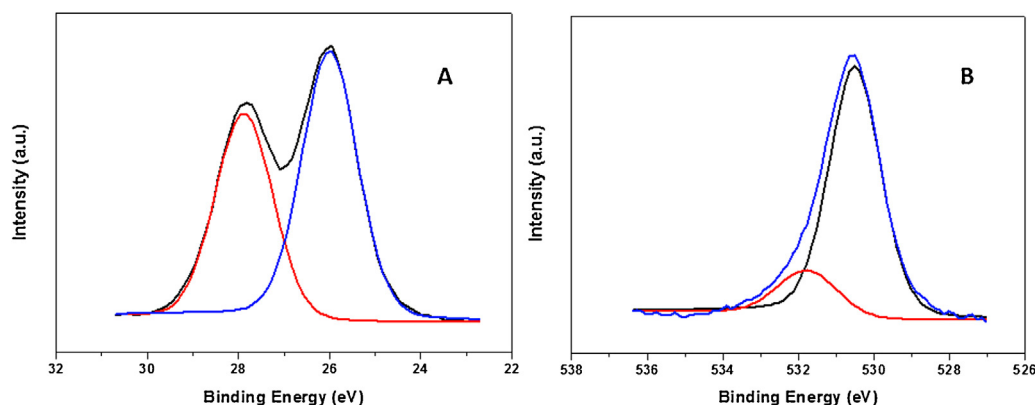

Fig. 5. Raman spectra of (A) mesoporous tantalum oxide and (B) bulk Ta$_2$O$_5$.

Fig. 7. (A) Ta 4f core level spectrum and (B) O 1s core level spectrum of mesoporous tantalum oxide.

subsequently dehydrated to HMF, mainly at medium temperatures; however, a partial participation of the direct transformation of glucose to HMF cannot be discarded. Although the maximum HMF yield (24.5%) is achieved at 185 °C, nevertheless, at 175 °C, the HMF selectivity and yield (23%) values are quite similar, so that this temperature was chosen to study the influence of other parameters on the catalytic reaction. The activity of this mesoporous Ta_2O_5 catalyst was expected since this solid exhibits a suitable acidity (353 μmol NH_3 g^{-1}). Considering that isomerisation of glucose to fructose implies the existence of Lewis acid sites [11,17], the evaluation of the concentration of both Brönsted and Lewis acid sites on mesoporous $Ta_2O_5 \cdot 0.19$ H_2O was performed by adsorption of pyridine coupled to FTIR spectroscopy (Fig. 9). Brönsted acid sites were not detected after heating this solid at 125 °C under vacuum, due to the elimination of most of coordinated water molecules, according to the TG study. In fact, under these conditions, its IR spectrum does not exhibit the band at 1600 cm^{-1} typical of OH groups. On these surface vacancies, pyridine molecules are bonded revealing to the formation of new Lewis acid centres. However, these acid sites are weak since when the sample is heated at 200 °C under vacuum, the band at 1450 cm^{-1} is largely reduced and completely disappears after evacuation at 300 °C (Fig. 9). The total concentration of Lewis acid centres is 98.1 μmol g^{-1}, as determined by using the extinction coefficients obtained by Datka et al. [33], $E_B = 0.73$ cm μmol^{-1} and $E_L = 1.11$ cm μmol^{-1}, for Brönsted and Lewis acid sites, respectively.

Nevertheless, in the catalytic reaction, both types of acid sites can participate owing to that catalyst was previously kept under a controlled humidity (55%), and so it can reabsorb some water molecules. This fact was confirmed by FTIR spectroscopy, which revealed the presence of water molecules and OH groups, as can be inferred from the vibration bands at 1600 and 3400 cm^{-1} (Fig. 6). To check the participation of Brönsted acid sites in this reaction, the mesoporous tantalum oxide has been treated with excess of KOH for 1 h and later washed with water till neutral pH, in order to neutralize all the Brönsted acid sites. This modified catalyst was then assayed under similar experimental conditions, leading to 54.7% of glucose conversion and 24.6% of HMF selectivity, which are lower values than those found with the pristine catalyst (69% of conversion and a HMF selectivity of 33%). As the resulting catalyst has not Brönsted acid centres, these catalytic results are assigned exclusively to the contribution of the Lewis acid sites; thus, the difference of activity with respect to the pristine one could be attributed to the participation of these Brönsted acid centres. This situation is different than that reported by Nakajima et al. [11] who found that
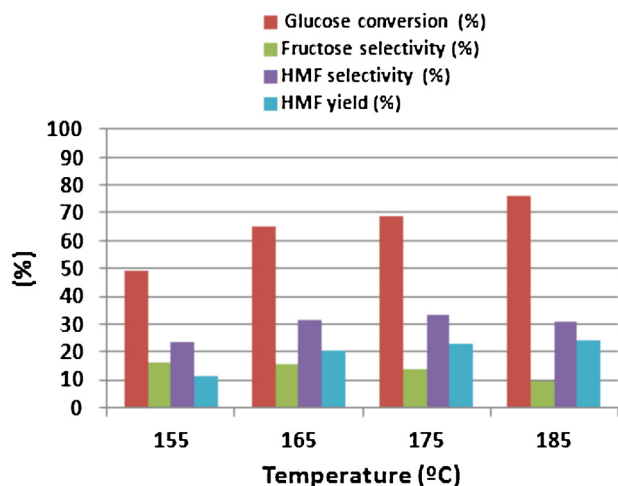

Fig. 8. Effect of the reaction temperature on the dehydration of glucose on mesoporous tantalum oxide: Reaction time = 90 min, mass of catalyst = 50 mg.
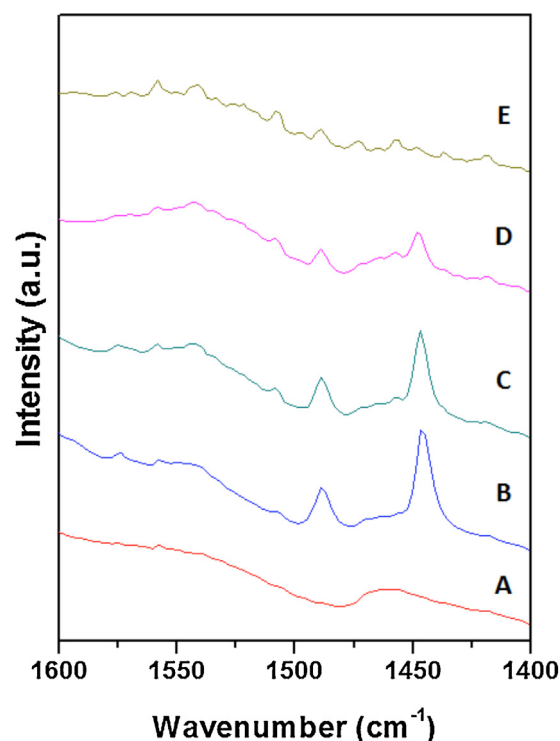

Fig. 9. FTIR spectra of mesoporous tantalum oxide: (A) evacuated at 125 °C. (B) Adsorbed pyridine at r.t., and (C) evacuated at 100 °C, (D) evacuated at 200 °C, (E) evacuated at 300 °C.
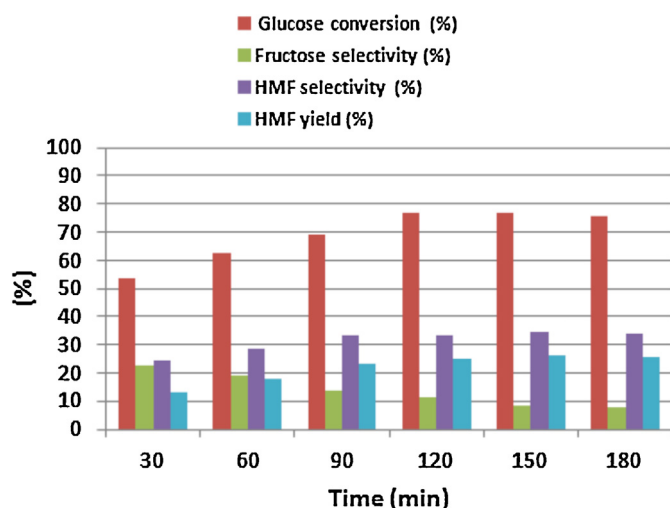
Fig. 10. Influence of the reaction time on the dehydration reaction of glucose. Reaction conditions: temperature = 175 °C, mass of catalysts = 50 mg.

Fig. 11. Evolution of the conversion of glucose, selectivity and yield of HMF as a function of the loading of catalyst. Reaction conditions: temperature = 175 °C, reaction time = 90 min.

there is no difference in HMF formation between $Nb_2O_5 \cdot nH_2O$ and $Na^+/Nb_2O_5 \cdot H_2O$, without Brönsted acid sites, which demonstrated the relevance of Lewis acid sites in HMF production from glucose in water. However, recently, a mechanism based on a synergy involving a Brönsted acid site and a nearby metal Lewis centre has been also proposed for the dehydration of glucose to HMF in a two-stage process on a niobium phosphate catalyst. In a first step, glucose isomerizes to fructose on Lewis acid sites and then fructose dehydrates to HMF on Brönsted acid sites, without desorption of fructose molecules [17].

The catalytic results reveal this solid as a selective catalyst for the production of HMF, since neither levulinic acid nor furfural were never detected. Therefore, although mesoporous tantalum oxide is a solid acid, its strength is not enough to produce the hydration of HMF to levulinic acid. In fact, when the catalyst was put in contact with HMF under similar experimental conditions (175 °C, 90 min) in the same biphasic system, levulinic acid was not detected. Moreover, all HMF could be recovered indicating that the formation of soluble polymers or humins do not take place; this could mean that these substances do not proceed directly from HMF but from the intermediates between glucose and HMF, as was reported by Kuster et al. [34]. This mechanism of humins formation through the condensation polymerization of 5-HMF with glucose has been also proposed recently by Dee and Bell [35]. However, kinetics and IR spectroscopy studies of the acid-catalysed conversion of HMF have led to bring forward other mechanistic pathway via reaction of HMF with 2,5-dioxo-6-hydroxy-hexanal, resulting from the hydration of HMF, and subsequent polimerisation [36]. Nevertheless, the full recovery of HMF in the above mentioned test, where water is present but glucose is not added to the reaction medium, could support the mechanism involving HMF and glucose. It must be highlighted that understanding the different processes involved in the degradation products formation in glucose dehydration still requires of considerable experimental and theoretical research, bearing in mind that the final goal is to minimize their negative influence on HMF yields.

The next step in the catalytic study was to evaluate the influence of the reaction time at 175 °C (Fig. 10). This reveals that the transformation of glucose to fructose is very fast, since 23% of fructose selectivity was achieved after 30 min, but at increasing reaction time, the selectivity toward fructose decreases owing to its transformation into HMF; however, a partial participation of the direct transformation of glucose to HMF can be also considered. The selectivity toward HMF increases with the reaction time,
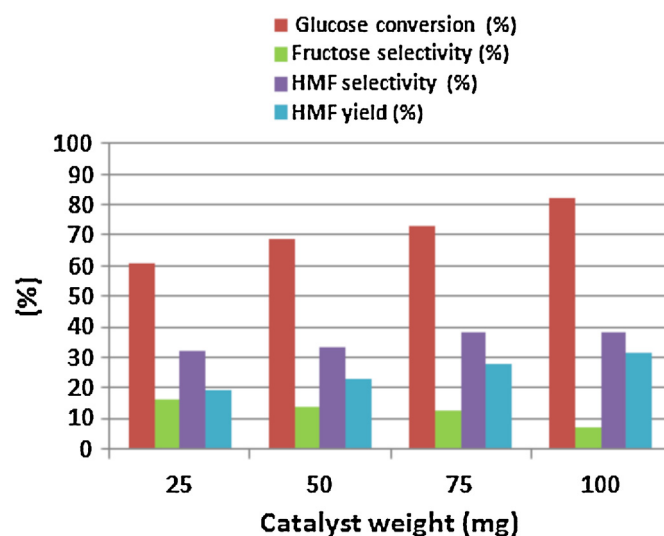
attaining the maximum value of 33% after 90 min. However, longer reaction times hardly improve the formation of HMF, possibly due to the preferential formation of soluble polymers and humins. Thus, this reaction time (90 min) was considered as optimal to study the influence of other parameters on the catalytic process.

The influence of the amount of catalyst on the catalytic reaction, at 175 °C and 90 min, shows that the glucose conversion monotonously increases with the weight of catalyst, but the HMF formation remains almost constant for catalysts loading higher than 75 mg, possibly due to the formation of a higher amount of condensation products from the intermediates of glucose/fructose with HMF or the acetalization of glucose with HMF in the aqueous medium (Fig. 11) [24]. Thus, the selectivity to HMF achieves the maximum value (38.5%) with 75 mg of catalyst; that means that the additional glucose converted in the presence of increasing amounts of catalyst is preferentially transformed into undesired products, such as soluble polymers and humins.

The results found in this work are different than those observed in the same reaction under similar experimental conditions, by using a mesoporous tantalum phosphate as catalyst [37]. Firstly, the catalytic activity is lesser for mesoporous tantalum oxide, since this catalyst leads to a glucose conversion of 69% and 23% of HMF yield, whereas the values for tantalum phosphate were 71% and 37.8%, respectively. These differences could be easily explained taking into account the acidity values of both catalysts. Thus, the total acidity for tantalum phosphate, as determined by ammonia TPD, was 1480 μmol g^{-1} whereas for mesoporous tantalum oxide is only 353 μmol g^{-1}. On the other hand, the strength of the acid sites of both catalysts is also different: all Brönsted acid sites of mesoporous tantalum oxide disappear after evacuation at 125 °C and Lewis acid sites are also weak strength, as inferred from its total elimination after desorption at 300 °C. However, tantalum phosphate exhibits strong Brönsted acid sites which are maintained even after evacuation at 375 °C [34]. However, the most important difference among both catalysts lies in their catalytic selectivity. Thus, mesoporous tantalum phosphate does not produce fructose as intermediate product, as least it is not detected among the reaction products. It is well established that the presence of basic sites or Lewis acid sites on the catalyst surface favors the isomerization of glucose to fructose, as a first step in this catalytic reaction. The adsorption of pyridine coupled to IR studies revealed, in the case of tantalum phosphate, the almost exclusive presence

of Brönsted acid sites ($C_B = 288\,\mu mol\,g^{-1}$ and $C_L = 36\,\mu mol\,g^{-1}$), so the catalytic reaction could take place preferentially through the direct transformation of glucose into HMF on Brönsted acid sites without previous isomerization to fructose. In any case, due to the presence of phosphate groups in the case of tantalum phosphate the mechanism proposed by Ordomsky et al. [17] could not be discarded, where glucose can be transformed into fructose over the scarce Lewis acid sites, accompanied by subsequent dehydration over nearby protonated phosphate groups without intermediate desorption of fructose molecules. In contrast, mesoporous tantalum oxide exhibits both kinds of acid sites; it must be stressed that this solid is still active in the catalytic reaction after neutralisation of all Brönsted acid sites by titration with excess of KOH, showing 54.7% of glucose conversion and 24.6% of HMF selectivity. Therefore, the presence of Lewis in this solid leads to the formation of fructose in great amount which is later transformed into HMF.

There are several papers in literature [11,14–17] dealing with the catalytic behavior of hydrated niobium oxide in the formation of HMF from dehydration of saccharides. Thus, the catalytic activity of this hydrated niobium oxide was moderate when the reaction is run at 120 °C over glucose as substrate [11], and it is lower than the results found with mesoporous $Ta_2O_5 \cdot 0.19\,H_2O$ studied in this work. Nevertheless, the performance of this amorphous oxide is largely enhanced when is treated with 1 M H_3PO_4 and calcined at 300 °C. On the other hand, the results obtained with mesoporous $Ta_2O_5 \cdot 0.19\,H_2O$ are even better than those described by using hydrated Nb_2O_5 or modified with phosphoric acid [17]. However, the use of hydrated tantalum oxide as catalyst in this field is very scarce. Only Yang et al. [18] have reported the performance of amorphous tantalum oxide in the preparation of HMF from fructose with good yield. When this amorphous oxide is treated with phosphoric acid and calcined at 300 °C, it is a very active catalyst for the preparation of HMF from glucose. However, the mesoporous solid studied in the present work, $Ta_2O_5 \cdot 0.19\,H_2O$, with very low amount of water per formula, after treatment with 1 M H_3PO_4 and calcined at 300 °C, does not improve the catalytic performance. This is a consequence of the low stability of the superficial esters formed between labile OH groups, coordinated to tantalum atoms, and phosphoric acid, which are destroyed during the thermal treatment at 300 °C. However, when the catalyst impregnated with H_3PO_4 is only dried at 85 °C for 2 h, and subsequently employed in the catalytic reaction for 120 min, a glucose conversion of 70.3% was attained, with 40.0% of HMF selectivity and, therefore, 28.1% of HMF yield. These results reveal that some phosphoric acid molecules are grafted on the mesoporous tantalum oxide, which are responsible of this increase of the activity. However the reuse of this catalyst without any treatment is not possible owing to the blocking of its narrow pores by insoluble polymers formed in the catalytic reaction; moreover, the analysis by ICP of the aqueous phase reveals leaching of phosphoric acid molecules since appear 17 ppm of phosphorus in this medium. However, the complete regeneration of the catalyst is achieved when, after calcinacion at 550 °C for 2 h, is again impregnated with phosphoric acid and dried at 85 °C.

The results found in the present study are also better than those reported by Watanabe et al. [38,39] by using other metallic oxides, like crystalline ZrO_2 as catalyst in the dehydration of glucose in hot compressed water at 200 °C. The same authors [40], using similar experimental conditions, but heating with microwave, achieved only a maximum HMF yield of 10%.

In conclusion, mesoporous tantalum oxide acts as a heterogeneous catalyst for the dehydration of glucose to HMF in a biphasic water/MIBK system at moderate temperature (175 °C) and in short reaction time (90 min), with high selectivity to HMF (33%) and with the absence of undesired side-reactions, since levulinic acid, formic acid and furfural were never found. The experimental conditions used in the present work make the process of glucose conversion into HMF environmentally friendly. Its catalytic activity could be correlated with the mesoporous structure and its surface area ($79\,m^2\,g^{-1}$) and porosity, suitable acidity ($353\,\mu mol\,NH_3\,g^{-1}$) and the presence of both types of acid sites (Lewis and Brönsted), both involved in the catalytic reaction.

Acknowledgments

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